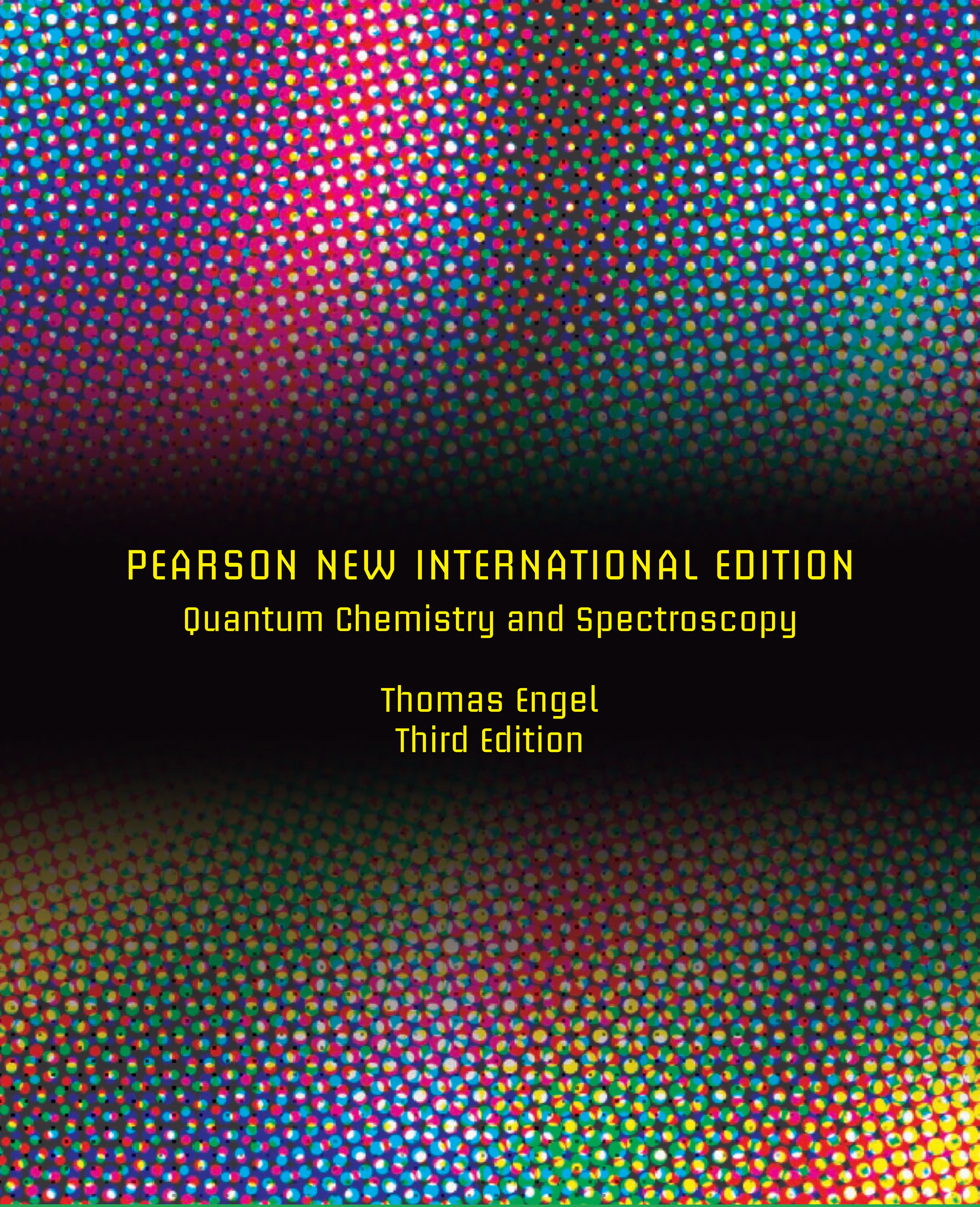

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Quantum Chemistry and Spectroscopy

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Note that this equation no longer contains partial derivatives. Because each side of the equation depends on only one of the variables and the equality exists for all values of the variables, it must be true that both sides of the equation are equal to the same constant:

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) + \beta\sin^2\theta = m_l^2 \quad \text{and}$$

$$\frac{1}{\Phi(\phi)}\frac{d^2\Phi(\phi)}{d\phi^2} = -m_l^2 \tag{49}$$

Looking back at the differential equation for rotation in two dimensions, it is clear why the constant is written in this way. The solutions for the second equation can be obtained immediately because the same equation was solved for the molecule rotating in two dimensions:

$$\Phi_+(\phi) = A_{+\phi}e^{i|m_l|\phi} \text{ and } \Phi_-(\phi) = A_{-\phi}e^{-i|m_l|\phi}, \quad \text{for } m_l = 0, 1, 2, 3, \ldots \tag{50}$$

where the part of $Y(\theta, \phi)$ that depends on ϕ is associated with the quantum number m_l.

The first equation in Equation (49) allows the part of $Y(\theta, \phi)$ that depends on θ to be determined. It can be solved to give a set of eigenfunctions and their corresponding eigenvalues. Rather than work through the solution, the results are summarized with a focus on the eigenvalues. A discussion of the spherical harmonics is postponed until Section 7. Two boundary conditions must be satisfied to solve Equation (49). To ensure that the functions $Y(\theta, \phi)$ are single-valued functions of θ and ϕ and that the amplitude of these functions remains finite everywhere, the following conditions must be met. We state rather than derive these conditions:

$$\beta = l(l+1), \quad \text{for } l = 0, 1, 2, 3, \ldots \quad \text{and}$$

$$m_l = -l, -(l-1), -(l-2), \ldots, 0, \ldots, (l-2), (l-1), l \tag{51}$$

Both l and m_l must be integers. Note that l and m_l are the quantum numbers for the three-dimensional rigid rotor. To emphasize this result, the spherical harmonic functions are written in the form

$$Y(\theta, \phi) = Y_l^{m_l}(\theta, \phi) = \Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi) \tag{52}$$

The function $\Theta_l^{m_l}(\theta)$ is associated with both quantum numbers l and m_l, and the function $\Phi_{m_l}(\phi)$ is associated only with the quantum number m_l. For a given value of l, there are $2l + 1$ different values of m_l ranging from $-l$ to $+l$. We next consider the origin of these quantum numbers more closely.

Why are there two quantum numbers for rotation in three dimensions, whereas there is only one for rotation in two dimensions? The answer is related to the dimensionality of the problem. For rotation in two dimensions, r was held constant. Therefore, ϕ is the only variable in the problem and there is only one boundary condition. For rotation in three dimensions, r is again held constant and, therefore, only the two boundary conditions on θ and ϕ generate quantum numbers. For the same reason, the particle in the one-dimensional box is characterized by a single quantum number, whereas three quantum numbers are required to characterize the particle in the three-dimensional box.

What observables of the rotating molecule are associated with the quantum numbers l and m_l? From the equation

$$\beta = \frac{2\mu r_0^2 E}{\hbar^2} = \frac{2I}{\hbar^2}E = l(l+1)$$

the energy eigenvalues for rotation in three dimensions can be obtained. This shows that the quantum number l is associated with the total energy observable,

$$E_l = \frac{\hbar^2}{2I}l(l+1), \quad \text{for } l = 0, 1, 2, 3, \ldots \tag{53}$$

and that the total energy eigenfunctions $Y_l^{m_l}(\theta, \phi)$ satisfy the eigenvalue equation

$$\hat{H}_{total}\,Y_l^{m_l}(\theta, \phi) = \frac{\hbar^2}{2I}l(l+1)Y_l^{m_l}(\theta, \phi), \quad \text{for } l = 0, 1, 2, 3, \ldots \tag{54}$$

Note that the rotational energy values are quantized and that, once again, the quantization arises through a boundary condition. Note that the energy levels depend differently on the quantum number than the energy levels for rotation in two dimensions for which

$$E_{m_l} = \frac{\hbar^2 m_l^2}{2\mu r_0^2} = \frac{\hbar^2 m_l^2}{2I}, \quad \text{for } m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{55}$$

For rotation in three dimensions the energy depends on the quantum number l, but not on m_l. Why is this the case? As will be shown in Section 7, the quantum number m_l determines the z component of the vector **l**. Because $\mathbf{E}_{total} = |\mathbf{l}|^2/2\mu r_0^2$, the energy of rotation depends only on the magnitude of the angular momentum and not its direction. Therefore, all $2l + 1$ total energy eigenfunctions that have the same l value but different m_l values have the same energy. This means that the **degeneracy** of each energy level is $2l + 1$. Recall that for rotation in two dimensions, the degeneracy of each energy level is two, except for the $m_l = 0$ level, which is nondegenerate.

6 The Quantization of Angular Momentum

We continue our discussion of three-dimensional rotation, although now it is discussed in the context of **angular momentum** rather than energy as was done earlier. Why is angular momentum important in quantum chemistry? Consider a familiar example from introductory chemistry, namely, the *s, p,* and *d* **orbitals** associated with atoms of the periodic table. We know that the bonding behavior of *s, p,* and *d* electrons is quite different. Why is an *s* orbital spherically symmetrical, whereas a *p* orbital has a dumbbell structure? Why are three energetically degenerate *p* orbitals directed along the *x, y,* and *z* directions? The origin of these chemically important properties is the particular value of l or m_l associated with these orbitals.

As discussed earlier, the spherical harmonic functions $Y_l^{m_l}(\theta, \phi)$, are eigenfunctions of the total energy operator for a molecule that rotates freely in three dimensions. Are these functions also eigenfunctions of other operators of interest to us? Because the potential energy is zero for a free rotor, the total energy stored in rotational motion is given by the kinetic energy $E_{total} = |\mathbf{l}|^2/2I$, in which **l** is the angular momentum and $I = \mu r_0^2$. Note that E_{total} and $|\mathbf{l}^2|$ differ only by the constant $1/2I$. Therefore, the corresponding operators $\hat{H}_{total}$ and $\hat{l}^2$ also satisfy this relationship. Because they differ only by a multiplicative constant, these two operators commute with one another and have a common set of eigenfunctions. Furthermore, because E_{total} is quantized, it can be concluded that $|\mathbf{l}^2|$ is also quantized. Using the proportionality of E_{total} and $|\mathbf{l}^2|$, the eigenvalue equation for the operator $\hat{l}^2$ can immediately be written from Equation (54):

$$\hat{l}^2 Y_l^{m_l}(\theta, \phi) = \hbar^2 l(l + 1) Y_l^{m_l}(\theta, \phi) \tag{56}$$

The notation explicitly shows that the quantum numbers l and m_l are defining indices for the eigenfunctions of $\hat{H}_{total}$ and $\hat{l}^2$. Because the eigenvalues for $\hat{l}^2$ are given by $\hbar^2 l(l + 1)$, the magnitude of the angular momentum takes on the quantized values $|\mathbf{l}| = \hbar\sqrt{l(l + 1)}$.

Note that it is $\hat{l}^2$and not $\hat{l}$ that commutes with $\hat{H}_{total}$. We now focus our attention on the angular momentum **l** and the corresponding operator $\hat{l}^2$. How many components does **l** have? For rotation in the xy plane, the angular momentum vector has only a single component that lies on the z axis. For rotation in three dimensions, the angular momentum vector has the three components l_x, l_y, and l_z, which are obtained from the vector cross product $\mathbf{l} = \mathbf{r} \times \mathbf{p}$. As might be expected from the discussion of the Stern–Gerlach experiment, the operators $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ do not commute.

As you will see when working the end-of-chapter problems, the operators $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ have the following form in Cartesian coordinates:

$$\hat{l}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$\hat{l}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$\hat{l}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{57}$$

Although not derived here, the operators have the following form in spherical coordinates:

$$\hat{l}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{l}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{l}_z = -i\hbar\left(\frac{\partial}{\partial\phi}\right) \tag{58}$$

As you will verify in the end-of-chapter problems for the operators in Cartesian coordinates, the commutators relating the operators $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ are given by

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$$
$$[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$$
$$[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y \tag{59}$$

Note that the order of the commutator is important, that is, $[\hat{l}_x, \hat{l}_y] = -[\hat{l}_y, \hat{l}_x]$.

What are the consequences of the fact that the operators corresponding to the components of the angular momentum do not commute with one another? Because the commutators are not zero, the direction of the angular momentum vector cannot be specified for rotation in three dimensions. To do so, it would be necessary to know all three components simultaneously, which would require that the three commutators in Equation (59) are zero. Given that $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ do not commute, what can be known about the components of the angular momentum for a molecule whose wave function is an eigenfunction of the total energy operator?

To answer this question, we look more closely at the operators for the individual components of the angular momentum. In spherical coordinates, $\hat{l}_x$ and $\hat{l}_y$ depend on both θ and ϕ, but as Equation (58) shows, $\hat{l}_z$ depends only on ϕ. As shown earlier, the spherical harmonics, $Y_l^{m_l}(\theta, \phi) = \Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi)$, are eigenfunctions of the total energy operator and of $\hat{l}^2$. We now show that the spherical harmonics are also eigenfunctions of $\hat{l}_z$. Applying $\hat{l}_z$ to the functions $Y_l^{m_l}(\theta, \phi)$, we obtain

$$\hat{l}_z(Y_l^{m_l}(\theta, \phi)) = \Theta(\theta)\left[-i\hbar\frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2\pi}}e^{im_l\phi}\right)\right] = m_l\hbar\Theta(\theta)\Phi(\phi),$$
$$\text{for } m_l = 0, \pm1, \pm2, \pm3, \ldots, \pm l \tag{60}$$

showing that the $Y_l^{m_l}(\theta, \phi)$ are eigenfunctions of $\hat{l}_z$. What can we conclude from Equation (60)? Because the spherical harmonics are eigenfunctions of both $\hat{l}^2$ and $\hat{l}_z$, both the magnitude of $|\mathbf{l}|$ and its z component can be known simultaneously. In other words, one can know the length of the vector **l** and one of its components, but it is not possible to simultaneously know the other two components of **l.**

Why has $\hat{l}_z$ rather than $\hat{l}_x$ or $\hat{l}_y$ been singled out, and what makes the z component special? There is nothing special about the z direction, and one could have just as easily chosen another direction. The way in which the variables are defined in spherical coordinates makes $\hat{l}_z$ take on a simple form. Therefore, when a direction is chosen, it is convenient to make it the z direction. The essence of the preceding discussion is that one can know the magnitude of **l** and only one of its components simultaneously.

The consequences of the different commutation relations among $\hat{H}$, $\hat{l}^2$, $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ are explored in Section 8, which deals with spatial quantization.

7 The Spherical Harmonic Functions

Until now, only the eigenvalues for $\hat{l}^2$, $\hat{H}$, and $\hat{l}_z$ for rotation in three dimensions have been discussed. We now discuss the spherical harmonic functions, $Y_l^{m_l}(\theta, \phi)$, which are the eigenfunctions common to these three operators. They are listed here for the first few values of l and m_l:

$$\begin{aligned}
Y_0^0(\theta,\phi) &= \frac{1}{(4\pi)^{1/2}} \\
Y_1^0(\theta,\phi) &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\
Y_1^{\pm 1}(\theta,\phi) &= \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi} \\
Y_2^0(\theta,\phi) &= \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \\
Y_2^{\pm 1}(\theta,\phi) &= \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{\pm i\phi} \\
Y_2^{\pm 2}(\theta,\phi) &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{\pm 2i\phi}
\end{aligned} \tag{61}$$

As seen earlier in Equation (50), the ϕ dependence is a simple exponential function. The θ dependence enters as a polynomial in $\sin\theta$ and $\cos\theta$. The numerical factor in front of these functions ensures that they are normalized over the intervals $0 \le \theta \le \pi$ and $0 \le \phi \le 2\pi$. Because the spherical harmonics are eigenfunctions of the time-independent Schrödinger equation, they represent standing waves on the surface of a sphere in which the nodal positions are independent of time.

For $l = 0$, the eigenfunction is equal to a constant determined by the normalization condition. What does this mean? Remember that the square of the wave function gives the probability density for finding the particle at the coordinates θ and ϕ within the interval $d\theta$ and $d\phi$. These coordinates specify the angle defining the internuclear axis in a diatomic molecule. If the wave function is independent of θ and ϕ, any orientation of the internuclear axis in the rotation of a molecule is equally likely. This must be the case for a state in which the angular momentum is zero. A net angular momentum, corresponding to $l > 0$, requires that the wave function and the probability density distribution not have spherical symmetry.

The spherical harmonics are complex functions unless $m_l = 0$. Graphing complex functions requires double the number of dimensions as for real functions, so that it is customary to instead form appropriate linear combinations of the $Y_l^{m_l}(\theta, \phi)$ to generate real functions. These functions, which still form an orthonormal set, are given in the following equations. Equation (62) lists the p functions, and Equation (63) lists the d functions. We recognize the abbreviations in connection with the orbital designations for the hydrogen atom. The functions shown in Figures 13 and 14 appear in the solutions of the Schrödinger equation for the hydrogen atom. Because of this, they merit more discussion.

$$\begin{aligned}
p_x &= \frac{1}{\sqrt{2}}\left(Y_1^1 + Y_1^{-1}\right) = \sqrt{\frac{3}{4\pi}} \sin\theta\cos\phi \\
p_y &= \frac{1}{\sqrt{2}\,i}\left(Y_1^1 - Y_1^{-1}\right) = \sqrt{\frac{3}{4\pi}} \sin\theta\sin\phi \\
p_z &= Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta
\end{aligned} \tag{62}$$

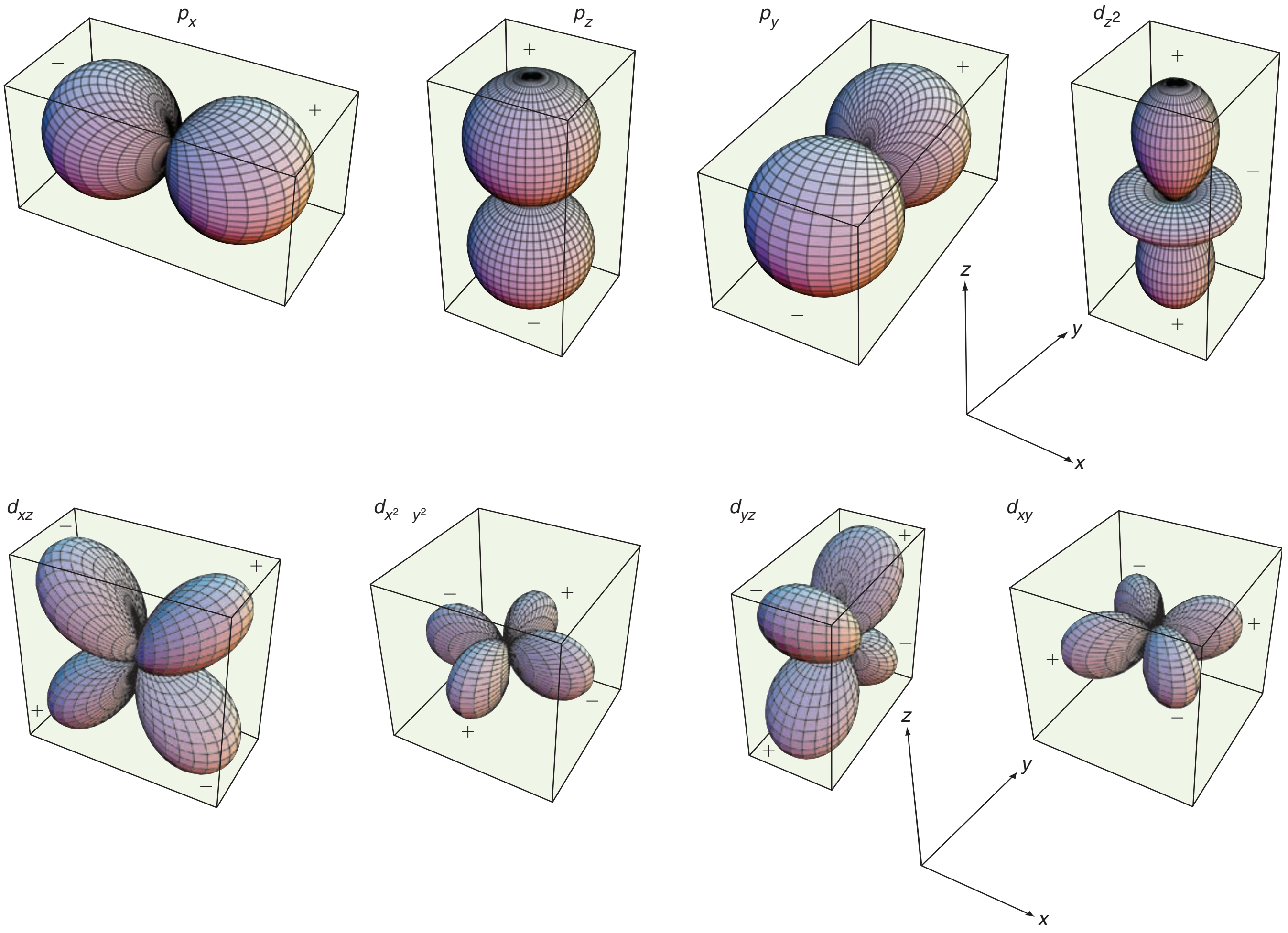

FIGURE 13
Three-dimensional perspective plots of the *p* and *d* linear combinations of the spherical harmonics. The plots show three-dimensional surfaces in which the relationship of the angles θ and ϕ to the Cartesian axes. The distance from the origin to a point on the surface (θ, ϕ) represents the absolute magnitude of the functions defined by Equations (62) and (63). The sign of the functions in the different lobes is indicated by plus and minus signs.

$$\begin{aligned}
d_{z^2} &= Y_2^1 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \\
d_{xz} &= \frac{1}{\sqrt{2}}\left(Y_2^1 + Y_2^{-1}\right) = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi \\
d_{yz} &= \frac{1}{\sqrt{2}\,i}\left(Y_2^1 - Y_2^{-1}\right) = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi \\
d_{x^2-y^2} &= \frac{1}{\sqrt{2}}\left(Y_2^2 + Y_2^{-2}\right) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi \\
d_{xy} &= \frac{1}{\sqrt{2}\,i}\left(Y_2^2 - Y_2^{-2}\right) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi
\end{aligned} \qquad \textbf{(63)}$$

These functions depend on two variables, θ and ϕ, and the way in which they are named refers them back to Cartesian coordinates. In graphing the functions, spherical coordinates have been used, whereby the radial coordinate is used to display the value of the amplitude, $r = f(\theta, \phi)$. All the functions generate lobular patterns in which the amplitude of the function in a lobe is either positive or negative. These signs are indicated in the plots.

The *p* functions form a set of three mutually perpendicular dumbbell structures. The wave function has the same amplitude but a different sign in the two lobes, and each function has a nodal plane passing through the origin. Four of the five *d* functions have a more complex four-lobed shape with nodal planes separating lobes in which the function has opposite signs. Because l is larger for the *d* than for the *p* functions, more nodes are seen in both angles. As for the particle in the box wave functions, an increase in the number of nodes corresponds to an increase in the energy of the quantum state. For the particle in the box, an increase in the number of nodes over a fixed interval corresponds to a shorter wavelength and, through the de Broglie relation, to a higher linear momentum. For the rigid rotor, an increase in the number of nodes over a fixed interval corresponds to a higher angular momentum.

Up to this point, questions have been asked about the energy and the momentum. What can be learned about the angular orientation of the internuclear axis for the rotating molecule? This information is given by the probability density, defined by the first postulate as the square of the magnitude of the wave function. The probability density for the *p* and *d* functions is very similar in shape to the wave function amplitude shown in Figure 13, although the amplitude in all lobes is positive. Taking the p_z plot as an example, Figure 13 shows that the maximum amplitude of $|Y_1^0|^2$ is found along the positive and negative z axis. A point on the z axis corresponds to the probability density for finding the molecular axis parallel to the z axis.

An alternate graphical representation can be used that recognizes that spherical harmonics can be used to represent waves on the surface of a sphere. This can be done by displaying the amplitude of the desired function on the sphere at the location θ, ϕ using a color scale. This is done in Figure 15, where the square of the amplitude of the p_z and p_y functions is plotted as a color scale on the surface of a sphere. Black and red regions correspond to high and low probability densities, respectively. For the p_z function, there is a much higher probability density of finding the particle near the z axis than in the $z = 0$ plane. This means that the molecular axis is much more likely to be parallel to the z axis than to lie in the xy plane. For a state whose wave function is p_y, the internuclear axis is much more likely to be parallel to the y axis than to lie in the $y = 0$ plane. This is consistent with the angular orientation of the maxima of these functions shown in Figure 13. Why is the probability density not more sharply peaked in a small angular region near the z or y axis? If the wave function is the p_z function, E_{total}, $|\mathbf{l}^2|$, and l_z are well defined. However, the operators for the angular coordinates ϕ and θ do not commute with the operators for E_{total}, $|\mathbf{l}^2|$, and l_z. As a consequence, the angular position coordinates are not known exactly and only average values can be determined for these observables.

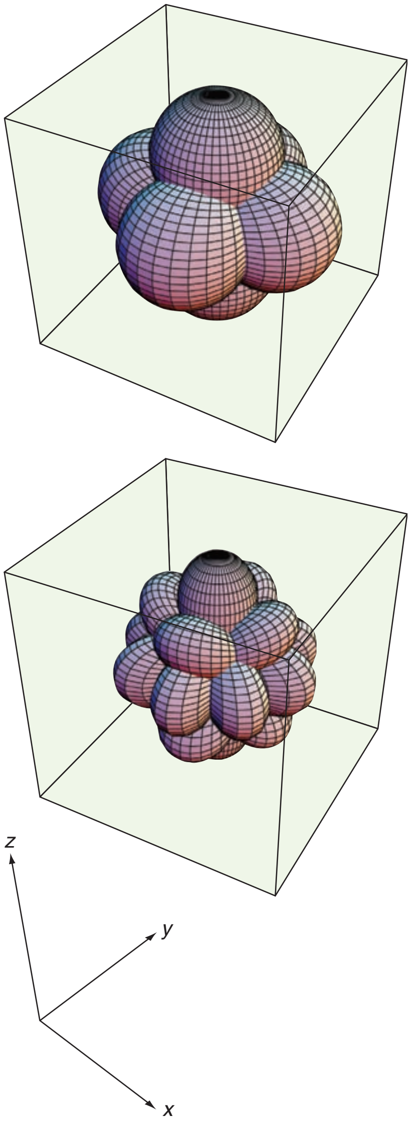

FIGURE 14
Three-dimensional perspective plots show the three *p* and the five *d* linear combinations of the spherical harmonics superimposed. The convention used in displaying the functions is explained in the text and in the caption for Figure 13.

8 Spatial Quantization

The fact that the operators $\hat{H}$, $\hat{l}^2$, and $\hat{l}_z$ commute whereas $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ do not commute with one another states that the energy, the magnitude of the angular momentum vector, and the value of any one of its components can be known simultaneously but that the other two components of the angular momentum cannot be known. Contrast this with classical mechanics in which all three components of an angular momentum vector can be specified simultaneously. In that case, both the length of the vector and its direction can be known.

We summarize what can be known about the angular momentum vector associated with a molecule rotating in three dimensions pictorially. In doing so, classical and quantum mechanical descriptions are mixed. For this reason, the following is a **semiclassical** description. The one component that is known is chosen to be along the z direction. In